

Study of Organic Molecules: Dye-Sensitized Solar Cells Application

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The organic molecules have important role in our life. The large applications of organic molecules are electronic and optical devices, consumer electronics and screens, clean energy devices, sensors, membranes, and light-harvesting antennas, among others. Finding and optimizing such materials for dye-sensitized solar cells (DSSCs) applications would be very helpful for the advancement of clean energy. In this work, a theoretical investigation was performed to examine some electronic and optical properties of some different organic dyes. We used the density functional theory (DFT) and time-dependent DFT (TD-DFT) methods with B3LYP functional and 6-31G basis set by using Gaussian 09 program to test some organic molecules by studying the UV-Vis spectrum, the electronic states transition and the range of the absorption spectrum. The improvement of dyes was done by the terminal addition with organic molecules where the absorption becomes higher than that of the original dyes and also the energy transition becomes lower in the DSSCs that use TiO₂ as a collector charge. Some electronic properties were done such as HOMO, LUMO distribution, energy gap, oscillator strength, and the geometrical optimization of these organic dyes. From these properties one can candidates these dyes as DSSCs.

Keywords: TD-DFT, organic molecules, organic solar cells, dye-sensitized, optoelectronic properties

1. Introduction

Organic solar cells are promising since carbon is one of the most abundant elements on earth [1]. Carbon bond has a good flexibility to alter the structure, which led to get various physical properties [2]. Solar cells are produced from light absorbing materials. The devices converting the energy of the sunlight into electricity by the photovoltaic effect discovered by the French scientist Henri Becquerel in 1839 [3]. Dye-sensitized solar cells (DSSCs) were invented by Michael Gratzel et al. also called dye solar cell or Grätzel cell, named after its inventor, who developed it in 1991 together with Brian O'Regan [4], it has generated a lot of interest leading to an exponential growth in research relating to DSSCs. The role of the dye is similar to the role of chlorophyll in plants [5,6]. The world energy demand is continuously, and the earth receives more than solar energy in 1 hour than is the energy used in 1 year globally, the solar power incidence, around 1 kW/m², and requires vast area of energy converters to cover the world's energy consumption [3,4]. The effected spectra of this type of solar cell has the range from 400 nm to 1300 nm i.e. 1 to 3 eV, which cover visible and infrared spectrum [7]. The dips prominently observed around 1100 nm, 1400 nm etc. due to absorption and from 200 nm to 400 nm due to scattering [3].

The photo physics of this system is based on highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the donor and acceptor materials which, in terms of light absorption, are conceptually similar to the conduction and valence band in an inorganic semiconductor. In organic materials the LUMOs and HOMOs levels do not interact strongly enough to form a conduction band and a valence band like in inorganic semiconductors [8]. The photo physics can be divided into four parts: absorption of light and generation of exciting, diffusion of exactions, dissociation of the exciting and generation of the charges, and charges transport and collection [4]. Organic solar cells are alternative to inorganic solar cells like silicon (Si); they can have extremely high optical absorption coefficients [9], DSSCs have also attracted much attention in recent years due to their advantages in low-cost manufacturing using inexpensive processes and are likely to be a significant contributor to the future commercial photovoltaic technology [10]. And thus a great deal of research work is currently being devoted to increase their power conversion efficiencies and scale-up production processes by modifying the chemical structure of the compounds [11]. Organic solar cells have reached confirmed power conversion efficiencies of over $11.2 \pm 0.3\%$, which is on a par with the latest DSSCs ($11.9 \pm 0.4\%$) [12]. The organic solar cells have two different electrodes. One of them must be transparent, usually indium tin oxide (ITO). The other electrode is very often aluminium (Al) [13,14]. Also, some reflection losses should be present, anti-reflection coatings and structured surface of the device can be used. [13,15]. In this work, we have studied the optimized geometries, optical, and electronic properties of some dyes used in dye-sensitive solar cells [16,17,18,19,20]. Improving these dyes with suitable additions has been done based on A. Irfan, and A. Mahmood [21]. The physical insight provided by computational modeling may help engineer new dyes and assess their performance. Many geometrical structure and electronic calculations have been done for various dye molecules, typically employing density functional theory (DFT) according to an accurately describe and less computational cost compared to other high-level quantum approaches as MP2, MP4 and also use time-dependent DFT (TD-DFT) for the absorption spectrum.

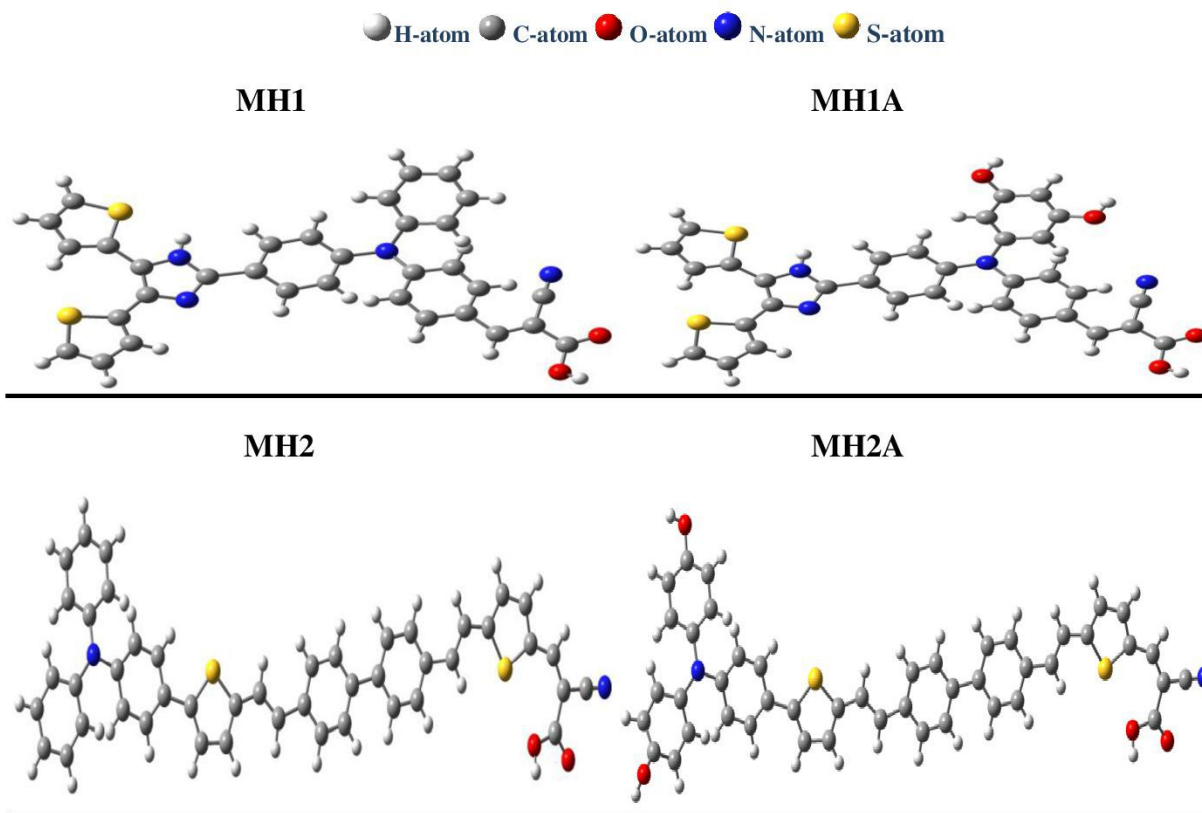
2. Computational Methodology

Geometrical structure and electronic properties of dyes have done by using DFT, which implemented in the Gaussian 09 program [22]. It was found in other works that the DFT-optimized geometries were excellent in agreement with the data obtained from experimental study [23]. Becke's three-parameter functional and Lee-Yang-Parr functional (B3LYP) [24] with the 6-31G basis set was used for all calculations [25]. The structures of dyes were optimized under no constraint, their properties as total energy (E_{total}), HOMO, LUMO energies, energy gap ($E_{gap} = E_{LUMO} - E_{HOMO}$), are examined. The open-circuit voltage $V_{OC} = E_{LUMO}^{Dye} - E_{LUMO}^{TiO_2}$ [17], the wavelengths, and the oscillator strengths (OS) have been investigated using TD-DFT calculations. Finally, the ultraviolet-visible (UV-Vis) absorption spectra of the dyes were simulated using Gauss View software [26].

3. Results and Discussion

3.1. Geometrical Structure Properties

The geometrical structures of investigated dyes of virtual name (MH1, MH2, MH3, MH4, MH5, MH1A, MH2A, MH3B, MH4B, and MH5C) which candidate to get high performance are shown in Fig.1. The optimization of this geometrical structures was obtained after the suitable addition of organic molecule (A, B, and C) as shown in Fig.2 in the suitable position using (DFT with B3LYP functional and 6-31G basis set) approach.



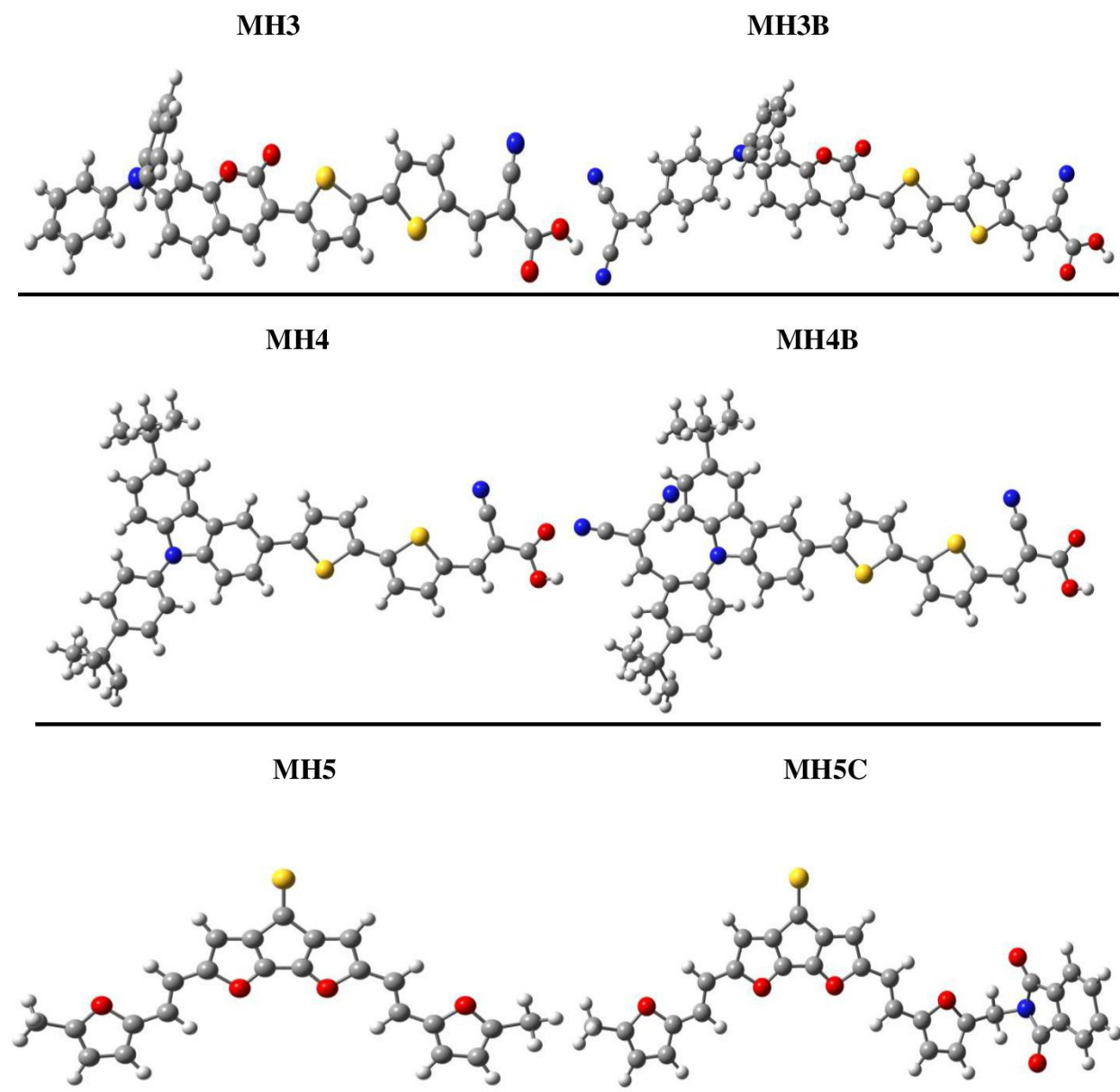


Fig.1. Geometrical optimization before (left) and after (right) addition of investigated dyes at B3LYP functional / 6-31G basis set.

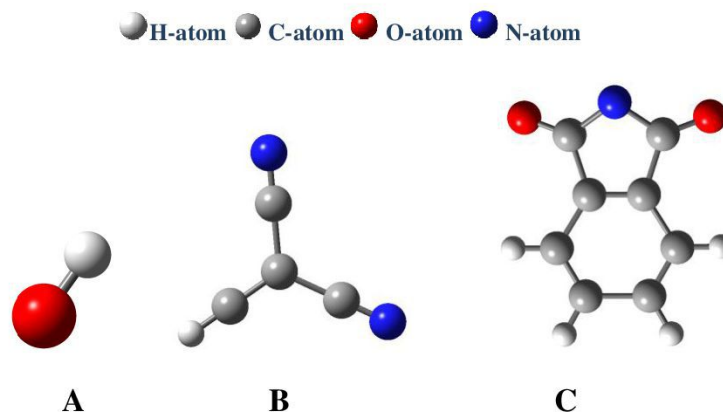
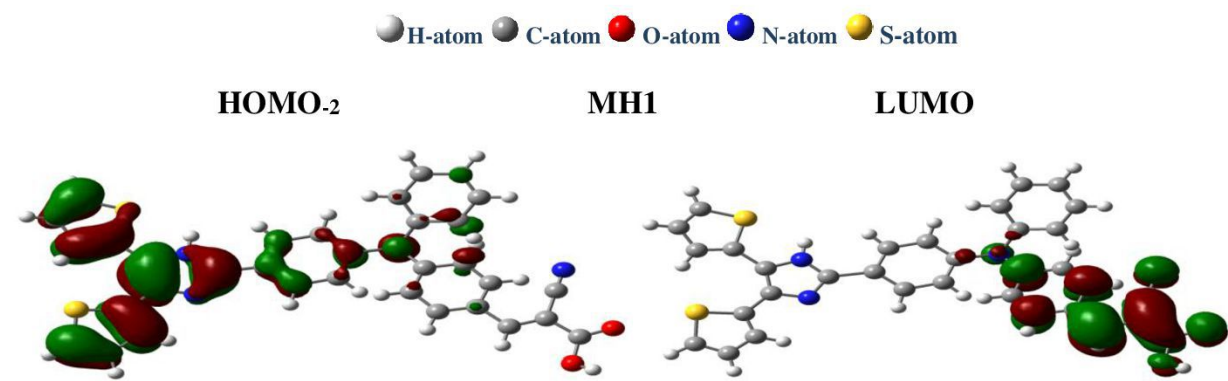


Fig.2. The three additions that use with dyes under study.

3.2. Electronic Properties

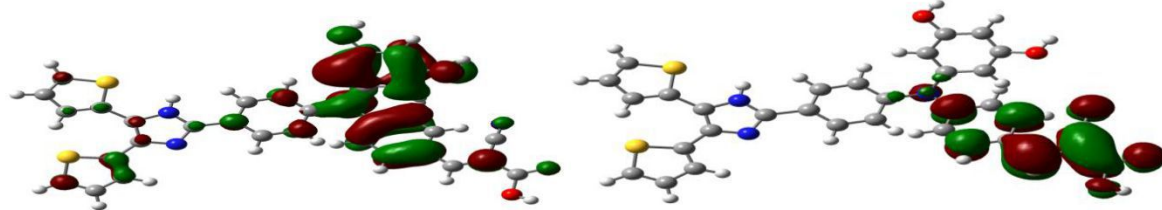
It is important to examine the HOMO and LUMO for these molecules. Based on the related references some dyes (dye MH1) have improved by adding two Hydroxyl molecules (two-A). [Fig.3](#) displays the difference between original HOMO₋₂ and HOMO₋₁ after addition whereas the electron still transfers from LUMO dye to LUMO (TiO₂) semiconductor. The original HOMO₋₂ distribution transfer from S atoms to OH molecules because OH they have high electronegativity. The (A) addition is also suitable for the dye MH2 and it has not effect on the electron transition i.e. electron still transfer from HOMO₋₂ to LUMO in both with or without addition. Another addition is famous organic molecules (B) was added, the electron transferring for dye MH3 was changed from (HOMO - LUMO) to (HOMO - LUMO₊₁) since the Nitrogen has electronegativity less than S and O. The next dye MH4 has small absorption and we use the same above addition (B), the original electronic transition is (HOMO₋₁ to LUMO) whereas (B) added the transition becomes from HOMO₋₁ to the different state LUMO₊₂. Which has large spatial orbital since the (B) position is locate far away from the O atoms as depicted. The famous acceptor is (C) since it has two O and one N atoms so the transition of the electron change from (HOMO - LUMO) to (HOMO - LUMO₊₂) which has large spatial orbital and this lead to the high OS for dye MH5C, the dye is considered to have proper energy levels as promising sensitizers in DSSCs.



HOMO-1

MH1A

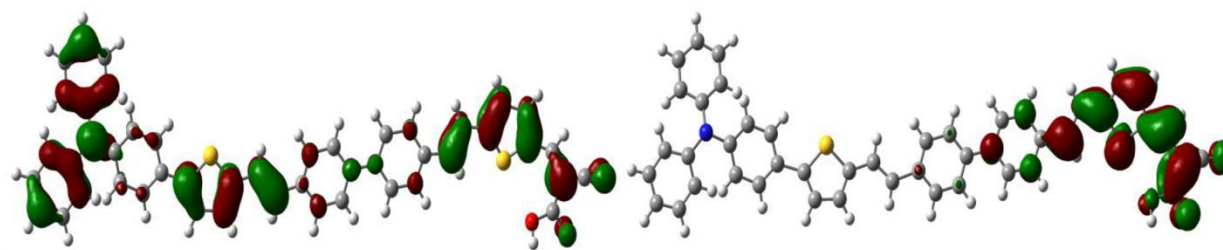
LUMO



HOMO-2

MH2

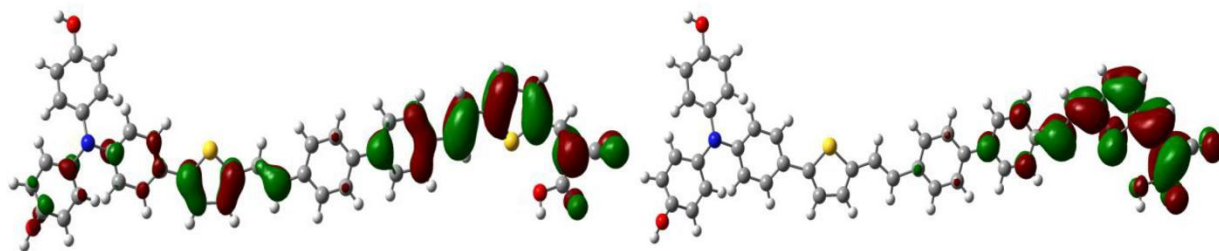
LUMO



HOMO-2

MH2A

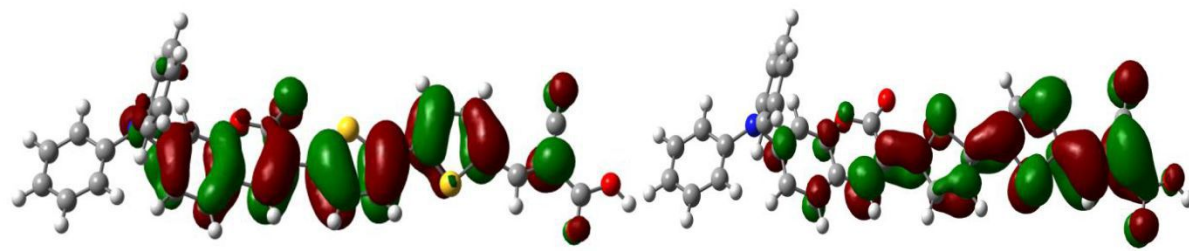
LUMO

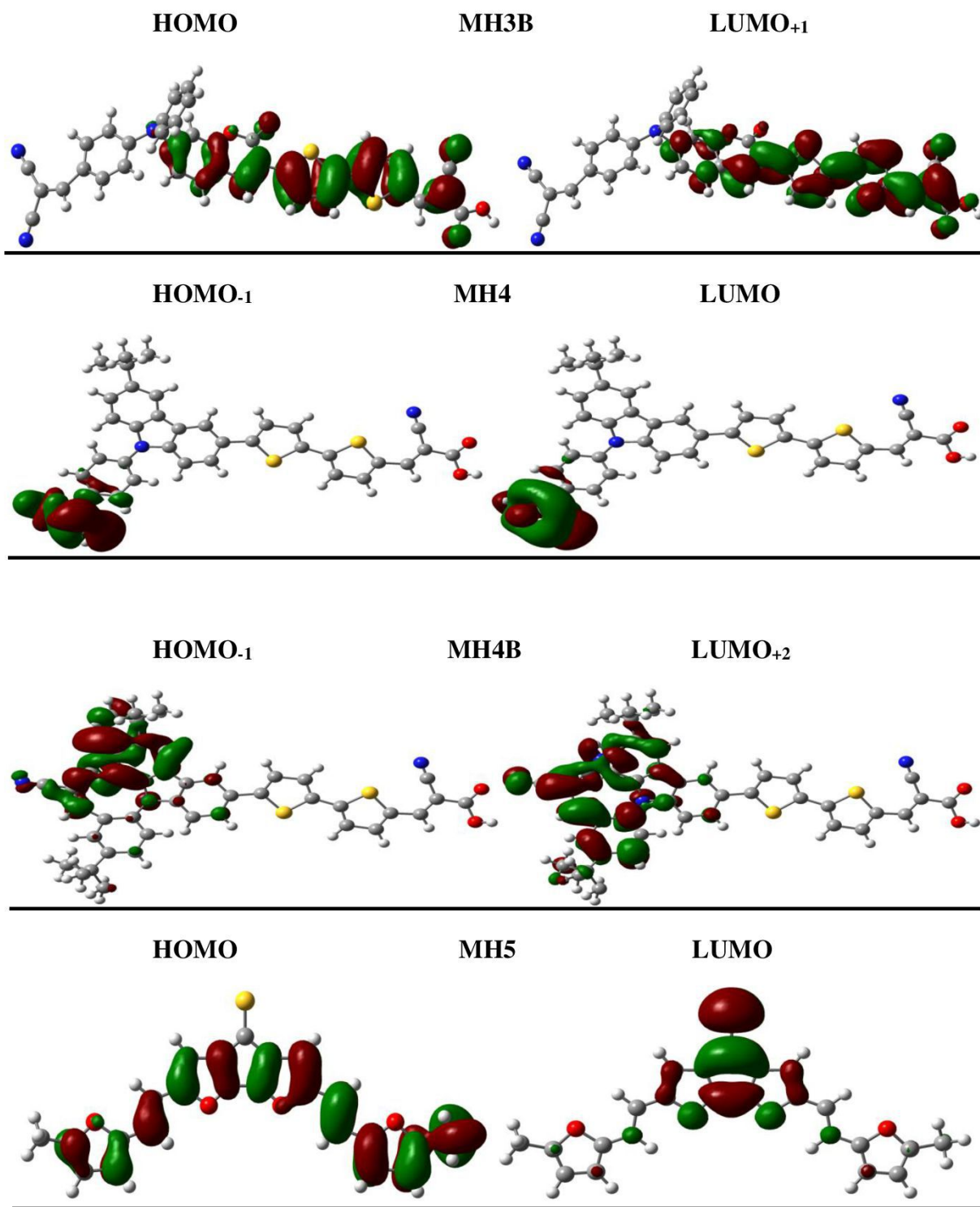


HOMO

MH3

LUMO





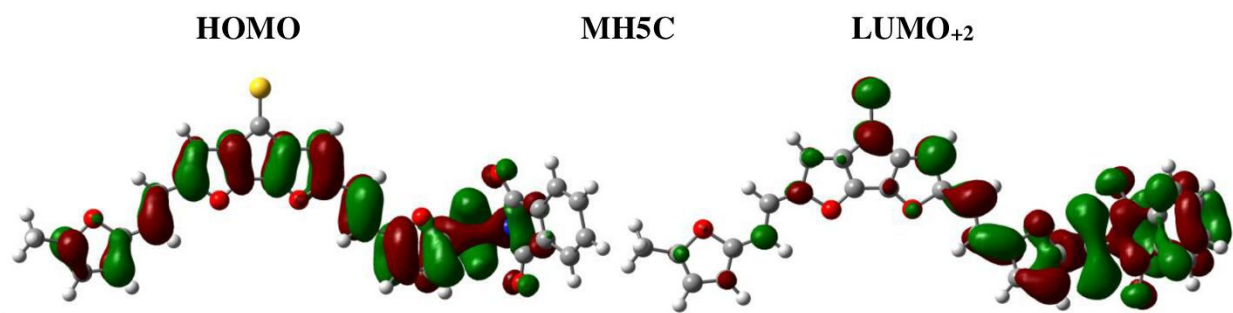


Fig.3. The localization of HOMO and LUMO before (left) and after (right) improvement of dyes

The HOMO, LUMO, E_{gap} , and E_{total} energies can be obtained by DFT calculations. When the total energy increase, this parameter would be of great importance of estimation of stability the structures. Therefore, the increase of E_{total} gives more stable and lower reactive for system.

Generally $LT = E_{LUMO}^{Dye} - E_{LUMO}^{TiO_2}$ and $HT = E_{LUMO}^{TiO_2} - E_{HOMO}^{Dye}$ have positive signal for all investigated dyes for ensuring the electronic injection from LUMO of dye to ($TiO_2 = -4.0$ eV) and HOMO of dye still lower than (TiO_2) energy. After addition, E_{gap} became small for dye MH1A, MH3B, and MH4B. Whereas E_{gap} became bigger for dye MH2B and MH5C. The band gaps values that calculated are in the range 1.39-3.87 eV. The range of the V_{OC} is from 0.93 to 1.88 eV, these values are sufficient for a possible efficient electron injection. The LT , HT , E_{total} , E_{gap} , and V_{OC} values of our studied molecules are listed in Table 1.

Table 1. Electronic properties parameters (HOMO (H-n), LUMO (L+n), E_{gap} , E_{total} , Electronic transition, LT , HT , and V_{OC}) obtained by B3LYP/6-31G for all dyes

Dye	H-n* (eV)	L+n* (eV)	E_{gap} (eV)	Electronic transition	E_{total} (eV)	LT (eV)	HT (eV)	V_{OC} (eV)
MH1	-6.41	-2.54	3.87	H-2->LUMO (74%)	-65923.91	1.46	2.41	1.46
MH1A	-5.98	-2.36	3.62	H-1->LUMO (90%)	-69999.06	1.64	1.98	1.64
MH2	-6.09	-3.07	3.02	H-2->LUMO (91%)	-76532.84	0.93	2.09	0.93
MH2A	-5.98	-2.93	3.05	H-2->LUMO (84%)	-80603.20	1.07	1.98	1.07
MH3	-5.76	-2.88	2.88	HOMO->LUMO (99%)	-67014.13	1.12	1.76	1.12
MH3B	-5.85	-3.04	2.81	HOMO->L+1 (98%)	-74099.68	0.96	1.85	0.96
MH4	-5.06	-2.81	2.25	H-1->LUMO (84%)	-68308.20	1.19	1.06	1.19
MH4B	-4.30	-2.12	2.18	H-1->L+2 (48%)	-75343.88	1.88	0.30	1.88
MH5	-4.18	-2.79	1.39	HOMO->LUMO	-42888.35	1.21	0.18	1.21

				(96%)				
				HOMO→L+2				
				(72%)				
MH5C	-4.36	-2.35	2.01		-56737.77	1.65	0.36	1.65

* H-n (n = 0,1,2,...); L+n (n = 0,1,2,...); n = 0, refers to basic HOMO and LUMO.

Based on the above presented results, the energy band structures are diagrammed in Fig. 4.

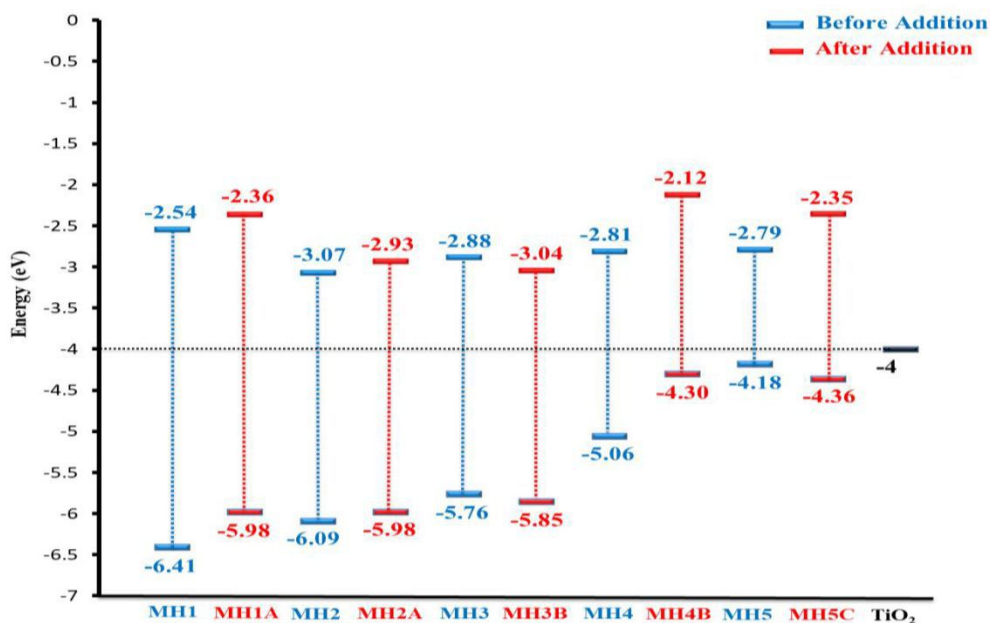


Fig. 4. HOMO and LUMO of dyes and TiO₂ energy levels (blue-plot before addition, red after)

3.3. Optical Properties

Based on the molecular structures optimized with the (DFT with B3LYP functional and 6-31G basis set), we calculated the UV-Vis spectra of the studied compounds using (TD-DFT with B3LYP functional and 6-31G basis set). Fig.5 a of dye MH1, illustrate the small λ_{max} shifted from 367 to 382 (nm) with the same range i.e. there is no range shift. Whereas the absorption from 12000 to 15000 as well as OS from 0.27 to 0.37 (eV). Either in the dye MH2 the absorption peak has increased from 73000 to 82000 with OS shift from 0.9140 to 1.6607 (eV) and exactly in the same range spectrum and same λ_{max} , as shown in Fig.5b. Fig.5c illustrate the increasing of the absorption for dye MH3 from 54000 to 70000 with some red-shifted. As we can see the λ_{max} has very small shifted from 473 to 476 (nm) with OS from 1.2 to 1.7 (eV). From Fig.5d, we observe that the λ_{max} for dye MH4 has very small shifted from 863 to 986 (nm) with OS from 0.0013 to 0.0030 (eV) whereas the absorption from 90 to 170 double of the original absorption. Also, we found out that dye MH5 (Fig. 5e), illustrate the increasing of the absorption from 2600 to 8300. In additional, the λ_{max} has shifted from 1392 to 838 (nm) with OS from 0.0492 to 0.1865 (eV). The absorbency in the same range has three times from 2000 to 8000. Finally, we summarized the data in Table 2.

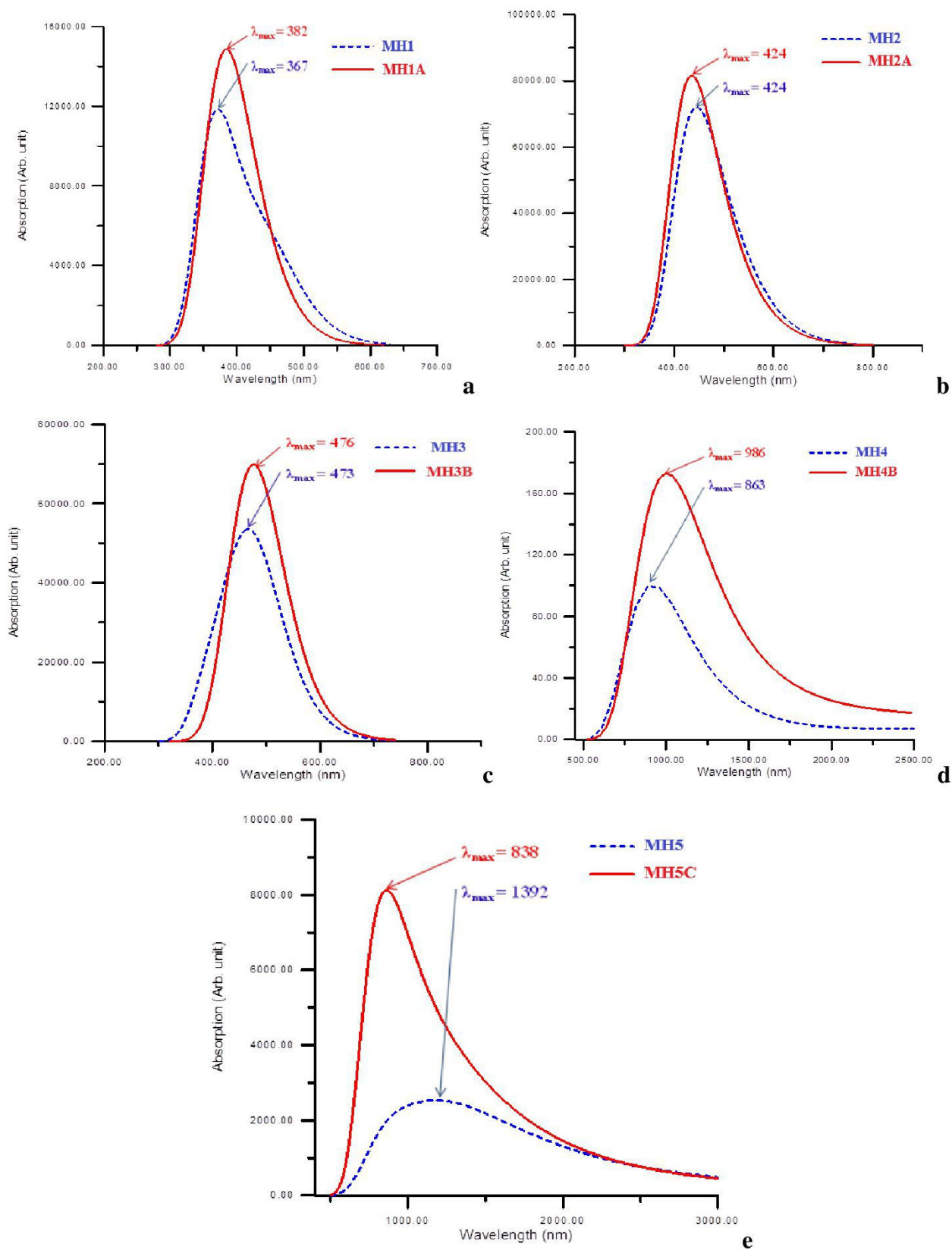


Fig. 5. The absorption spectra of dyes before (blue line) and after (red line)

Table 2. Data absorption spectra obtained by TD-DFT method with B3LYP/6-31G for all dyes

Dye	λ_{max} (nm)	OS (eV)
MH1	367	0.2765
MH1A	382	0.3717
MH2	424	0.9140
MH2A	424	1.6607
MH3	473	1.2225
MH3B	476	1.7194
MH4	863	0.0013
MH4B	986	0.0030
MH5	1392	0.0492
MH5C	838	0.1865

We have dealt in the discussion with the important properties that control on the DSSCs performance such as HOMO, LUMO, E_{gap} , E_{total} , LT , HT , V_{OC} , λ_{max} , OS, electronic transition beside the orbital spatial localization, and the UV-Vis spectra in order to study deeply how the additions type are suitable to get high DSSCs performance.

4. Conclusions

In this work, the optimized geometries, electronic, and optical properties of dyes MH1, MH2, MH3, MH4, MH5, MH1A, MH2A, MH3B, MH4B, and MH5C were investigated by using DFT and TD-DFT in order to display the influence of molecular structure on the electronic and optical properties of these materials. The standard dyes under this study can be improved by adding the suitable terminal organic molecules. The energy gaps differ from 1.39 to 3.87 eV depending on the addition. After addition, E_{gap} decreased for dye MH1A, MH3B, and MH4B. Whereas E_{gap} increased for dye MH2A and MH5C. The total energy increased in all modification dyes after addition, this refers to high stable. The changing of the transition states after the improvement gives low energy that need, as comparison with the original dyes. The calculated values of V_{OC}/TiO_2 of our dyes are sufficient for a possible efficient electron injection from the donor to the acceptor. All dyes, which under study can be used as sensitizers because the electron injection process from the excited molecule to the conduction band of TiO_2 are feasible in the organic sensitized solar cell. The LUMO of modification dyes stills higher than that of TiO_2 with high efficient charge transfer. The terminal additions that have nitrogen reveal to the high efficiency of the DSSCs. Presently the addition (C) was very suitable for rising the absorption to three times when compared with original dye. Finally, theoretical calculations can be used to predict electronic and optical properties of some dyes and further to design promising sensitized organic solar cells.

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